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The Crystal Structure of a 1,4-Etheno-2,8-diacetoxy-2,4,6,8-tetramethyloctahydronaphthal-5-ene-3,7-dione

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The Diels-Alder product 1,4-etheno-2,8-diacetoxy-2,4,6,8-tetramethyloctahydronaphthal-5-ene-3,7-dione is a dimer of 6-acetoxy-2,6-dimethyl-2,4-cyclohexadienone which is formed upon lead tetraacetate oxidation of 2,6-dimethylphenol. A determination of the crystal structure of the dimer shows that it has *endo* configuration and that two enantiomeric molecules have dimerised. The structure is rather strained with $C(sp^3)-C(sp^3)$ bond lengths of 1.591 and 1.553 Å for the bonds C(4) – C(4a) and C(4a) – C(8a), respectively.

The structure was determined by direct methods from counter intensities. The crystals are monoclinic, space group $P2_1/c$, with $a=11.442$, $b=10.841$, $c=14.718$ Å, $\beta=95.11°$ and $Z=4$. The final R value was 0.045 for 2454 reflexions.

Oxidation of methyl homologues of *o*-cresol with sodium periodate results in the formation of *o*-quinols which generally undergo rapid Diels-Alder dimerisation to give substituted 1,4-ethenonaphthalenes.[1,2] Oxidation with lead tetraacetate gives *o*-quinol acetates which similarly dimerise at 120 °C.[3]

Oxidation of 2,6-dimethylphenol with lead tetraacetate gives as the main product 6-acetoxy-2,6-dimethyl-2,4-cyclohexadienone. Dimeric *o*-quinol acetates are formed at 120 °C and 165 °C, respectively. The title compound is the stereoisomer formed at 165 °C.[4]

This X-ray investigation, within a program of crystal-structure studies of Diels-Alder adducts of *o*-quinols, has been undertaken primarily to determine whether the configuration of the dimer is *endo* or *exo* and to establish the steric arrangement at the asymmetric carbon atoms.

EXPERIMENTAL

Cell dimensions were obtained from a least-squares treatment of the angular positions of 25 accurately centered reflexions as measured on the computer-controlled Philips PW 1100 diffractometer. Crystal data are: space group $P2_1/c$, $a=11.442(1)$, $b=10.841(2)$, $c=14.718(2)$ Å, $\beta=95.11(2)°$ $V=1818.4$ Å^3, $Z=4$, $D_c=1.316$ g cm^{-3}.

Intensity data were collected to a 2θ value of 130° by the $\omega-2\theta$ scan technique with graphite monochromatized Cu$K\alpha$ radiation. The intensities of 3102 independent reflexions were measured. Backgrounds were estimated by stationary counting at $2\theta \pm 0.75°$ from the peak maxima. The scan speed was 0.015° s^{-1}. Three standard reflexions were measured every 90 min. No systematic variation was detected. All reflexions with net intensity $I<4\sigma(I)$, where $\sigma(I)$ is standard deviation estimated from counter statistics, were ignored. The remaining 2454 independent reflexions were used in the refinement of the structure. Lorentz and polarization factors were applied, but not absorption corrections.

STRUCTURE DETERMINATION AND REFINEMENT

The structure factor phases were determined by direct methods. Normalized $|E|$'s were calculated from structure amplitudes on approximately absolute scale and from the Wilson[5] average temperature factor. Phase determination by "variance-weighted" $\sum_2$-relationships[6] was restricted to the 245 reflexions with $|E|>1.75$. Eight trial phase sets were generated from starting sets consisting of three origin reflexions and three reflexions as variables. An E map computed from 204 well-phased

Table 1. Positional and anisotropic thermal parameters of the non-hydrogen atoms. The β-values refer to the temperature factor expression $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$. Estimated standard deviations are given in parentheses. Values are $\times 10^4$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1476(2)	3293(2)	2752(2)	49(2)	56(2)	45(1)	−4(3)	20(2)	−7(2)
C(2)	831(2)	4538(2)	2580(2)	51(2)	63(2)	44(1)	7(3)	24(2)	5(2)
C(3)	1151(2)	5346(2)	3424(2)	70(2)	61(2)	43(1)	25(3)	40(2)	4(2)
C(4)	1957(2)	4725(2)	4171(2)	76(2)	63(2)	38(1)	26(3)	37(2)	−3(2)
C(4a)	3127(2)	4328(2)	3740(2)	61(2)	51(2)	36(1)	−7(3)	22(2)	−7(2)
C(5)	3906(2)	3674(2)	4462(2)	66(2)	82(2)	35(1)	3(3)	10(2)	−17(3)
C(6)	4140(2)	2470(2)	4479(2)	68(2)	84(2)	33(1)	25(3)	21(2)	5(2)
C(7)	3656(2)	1718(2)	3696(2)	57(2)	57(2)	42(1)	19(3)	34(2)	8(2)
C(8)	3580(2)	2410(2)	2785(2)	47(2)	55(2)	35(1)	−1(3)	22(2)	−5(2)
C(8a)	2809(2)	3571(2)	2857(2)	49(2)	50(2)	33(1)	−1(3)	21(2)	0(2)
C(9)	1095(2)	2815(2)	3644(2)	63(2)	59(2)	62(2)	0(3)	50(3)	24(3)
C(10)	1321(2)	3541(2)	4354(2)	80(2)	76(2)	48(2)	32(3)	61(3)	27(3)
C(11)	−491(2)	4389(3)	2391(2)	51(2)	99(3)	69(2)	15(4)	24(3)	16(4)
O(12)	1286(1)	5286(2)	1863(1)	61(1)	66(2)	40(1)	4(2)	14(2)	5(2)
C(13)	1295(2)	4846(2)	1005(2)	60(2)	89(2)	40(1)	13(3)	4(2)	−12(3)
O(14)	968(2)	3835(2)	778(2)	141(2)	107(2)	55(1)	−33(3)	18(3)	−39(2)
C(15)	1763(3)	5788(3)	399(2)	93(3)	125(3)	42(2)	−8(5)	22(3)	10(3)
O(16)	764(2)	6370(2)	3488(2)	149(2)	81(2)	60(1)	103(3)	13(3)	−10(2)
C(17)	2181(3)	5568(3)	4996(2)	131(3)	87(3)	40(1)	60(5)	27(3)	−22(3)
C(18)	4839(3)	1818(3)	5248(2)	111(3)	136(4)	40(2)	97(5)	13(3)	18(4)
O(19)	3301(2)	672(2)	3763(1)	100(2)	66(2)	61(1)	−1(3)	54(2)	21(2)
C(20)	3202(2)	1592(2)	1980(2)	63(2)	71(2)	42(1)	−3(3)	23(2)	−25(3)
O(21)	4722(1)	2966(1)	2644(1)	50(1)	64(2)	38(1)	1(2)	24(2)	1(2)
C(22)	5689(2)	2261(2)	2766(2)	53(2)	66(2)	40(1)	14(3)	16(2)	−10(2)
O(23)	5681(2)	1209(2)	3020(2)	67(2)	79(2)	89(2)	29(2)	35(2)	22(2)
C(24)	6750(2)	2955(3)	2558(2)	52(2)	94(3)	65(2)	0(4)	18(3)	9(3)

Table 2. Positional parameters ($\times 10^3$) of the hydrogen atoms. Estimated standard deviations are given in parentheses.

Atom	x	y	z	B Å^2
H(1)	127(2)	276(2)	228(2)	2827
H(4a)	353(2)	504(2)	357(2)	3025
H(5)	426(2)	422(2)	498(2)	3299
H(8a)	301(2)	408(2)	234(2)	2478
H(9)	69(2)	209(2)	365(2)	3457
H(10)	109(2)	337(2)	494(2)	3711
H1(11)	−67(2)	388(3)	185(2)	4236
H2(11)	−74(3)	403(3)	291(2)	4236
H3(11)	−85(3)	516(3)	226(2)	4236
H1(15)	200(3)	544(3)	−9(2)	4689
H2(15)	242(3)	618(3)	66(2)	4689
H3(15)	121(3)	636(3)	29(2)	4689
H1(17)	267(3)	627(3)	483(2)	4525
H2(17)	147(3)	591(3)	521(2)	4525
H3(17)	266(3)	518(3)	550(2)	4525
H1(18)	516(3)	246(3)	567(2)	4998
H2(18)	544(3)	139(3)	504(2)	4998
H3(18)	434(3)	130(3)	555(2)	4998
H1(20)	307(2)	206(3)	148(2)	3466
H2(20)	249(2)	119(2)	207(2)	3466
H3(20)	379(2)	100(2)	190(2)	3466
H1(24)	703(2)	334(3)	309(2)	3926
H2(24)	659(3)	349(3)	218(2)	3926
H3(24)	737(3)	247(3)	249(2)	3926

reflexions displayed all the non-hydrogen atoms as the prominent peaks. The structure was refined by the full-matrix least-squares method. When the R value reached 0.084 with anisotropic temperature factors, a difference synthesis was calculated. This revealed all the hydrogen atoms. The hydrogen atoms were given the final isotropic thermal parameters of the atoms to which they are attached and only the positional parameters were included in further refinement. The R value reduced to 0.045. Scattering factors for C and O were those of Freeman [7] and for H, those of Stewart, Davidson and Simpson.[8] Hughes [9] weighting procedure with $F_{o,min}=3.0$ was applied. The final positional and thermal parameters are given in Tables 1 and 2. A list of the observed and calculated structure factors is available from the authors on request.

RESULTS AND DISCUSSION

A view of the crystal structure in Fig. 1 shows that the dimerisation has followed the

Table 3. Bond angles (°) involving non-hydrogen atoms, with estimated standard deviations in parentheses.

C(2) – C(1) – C(8a)	107.3(2)
C(2) – C(1) – C(9)	105.7(2)
C(8a) – C(1) – C(9)	109.8(2)
C(1) – C(2) – C(3)	106.8(2)
C(1) – C(2) – C(11)	112.9(2)
C(1) – C(2) – O(12)	114.0(2)
C(3) – C(2) – C(11)	111.7(2)
C(3) – C(2) – O(12)	101.1(2)
C(11) – C(2) – O(12)	109.8(2)
C(2) – C(3) – C(4)	114.6(2)
C(2) – C(3) – O(16)	121.8(2)
C(4) – C(3) – O(16)	123.6(2)
C(3) – C(4) – C(4a)	107.9(2)
C(3) – C(4) – C(10)	103.4(2)
C(3) – C(4) – C(17)	111.0(2)
C(4a) – C(4) – C(10)	106.1(2)
C(4a) – C(4) – C(17)	113.1(2)
C(10) – C(4) – C(17)	114.7(2)
C(4) – C(4a) – C(5)	108.2(2)
C(4) – C(4a) – C(8a)	109.5(2)
C(5) – C(4a) – C(8a)	115.0(2)
C(4a) – C(5) – C(6)	125.5(2)
C(5) – C(6) – C(7)	117.7(2)
C(5) – C(6) – C(18)	124.5(3)
C(7) – C(6) – C(18)	117.7(2)
C(6) – C(7) – C(8)	113.6(2)
C(6) – C(7) – O(19)	123.9(2)
C(8) – C(7) – O(19)	122.4(2)
C(7) – C(8) – C(8a)	109.1(2)
C(7) – C(8) – C(20)	112.8(2)
C(7) – C(8) – O(21)	110.0(2)
C(8a) – C(8) – C(20)	114.0(2)
C(8a) – C(8) – O(21)	101.3(2)
C(20) – C(8) – O(21)	109.0(2)
C(1) – C(8a) – C(4a)	110.0(2)
C(1) – C(8a) – C(8)	113.4(2)
C(4a) – C(8a) – C(8)	113.3(2)
C(1) – C(9) – C(10)	115.6(2)
C(4) – C(10) – C(9)	115.5(2)
C(2) – O(12) – C(13)	120.8(2)
O(12) – C(13) – O(14)	123.7(2)
O(12) – C(13) – C(15)	110.6(2)
O(14) – C(13) – C(15)	125.7(3)
C(8) – O(21) – C(22)	118.7(2)
O(21) – C(22) – O(23)	123.5(2)
O(21) – C(22) – C(24)	111.4(2)
O(23) – C(22) – C(24)	125.1(2)

endo addition rule. The configuration at carbon atom C(8) is different from that found in X-ray investigations of related compounds.[10–12] This is probably due to steric requirements since the rather bulky acetoxy group has replaced a hydroxyl group [10,11] or a chlorine.[12] Here again, the bulkiest group on carbon atom C(8) is oriented away from the reaction center.

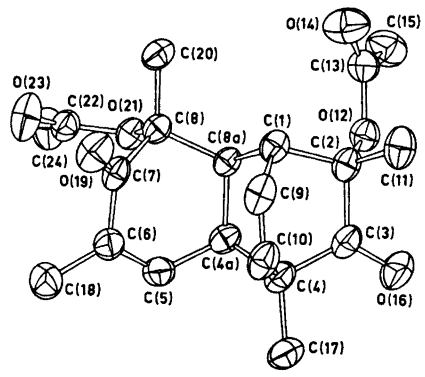

Fig. 1. A perspective view of the molecule.

Intramolecular bond distances are given in Fig. 2 and bond angles involving non-hydrogen atoms in Table 3. No corrections for thermal motion have been applied. Most bond lengths in this structure agree with those observed in similar structure;[10–12] the bond C(4) – C(4a) (1.591 Å) is again significantly longer than the mean value, 1.536 Å, of the other C(sp^3) – C(sp^3) bonds in the structure.

The four atoms C(4a), C(5), C(6), and C(7) in the cyclohexene ring are coplanar within 0.017 Å. Atoms C(8) and C(8a) deviate 0.832 and 0.260 Å from the plane, respectively. The three rings containing the etheno moiety are all boat-shaped.

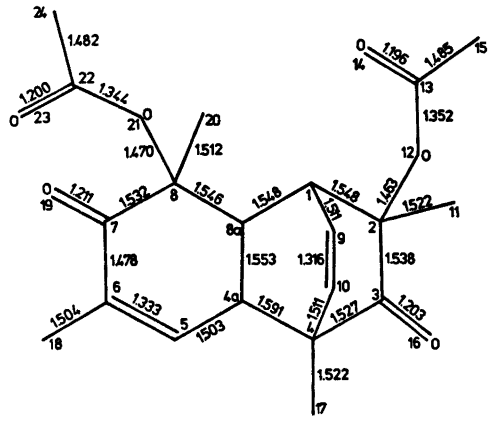

Fig. 2. Bond distances in the molecule. Standard deviations are estimated to be 0.003 Å.

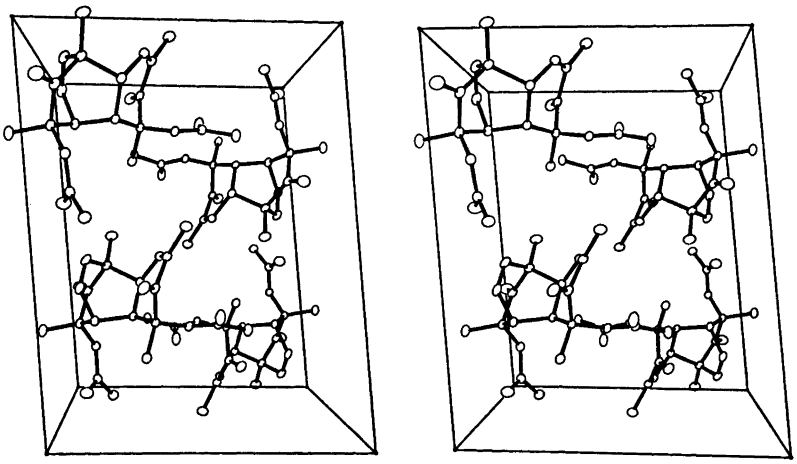

Fig. 3. A stereoscopic view of the molecular packing.

The arrangement of molecules in the unit cell is shown in Fig. 3. All intermolecular contacts are normal van der Waals distances.

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